

**In the Title**

Kindly change the Title to -- Surface-Treated Steel Sheet and Method for Manufacturing the  
Same --.

### In the Specification

*Kindly replace paragraph [0001] with the following:*

[0001] ~~The present invention~~ This disclosure relates to a surface treated steel sheet exhibiting excellent corrosion resistance and surface appearance and containing no chromium in a surface treatment film, as well as a method for manufacturing the same. The steel sheet ~~of the present invention~~ is widely used for automobiles, household electrical appliances, construction materials, and the like.

*Kindly replace paragraphs [0013] and [0014] with the following:*

[0013] ~~The present invention was made to overcome the above-described problems. Accordingly, it is an object of the present invention~~ It could therefore be helpful to provide a surface treated steel sheet containing no chromium in a film and exhibiting excellent corrosion resistance and surface appearance, as well as a method for manufacturing the same. Furthermore, a surface treated steel sheet exhibiting excellent workability in addition to the corrosion resistance and the surface appearance, as well as a method for manufacturing the same, is provided.

#### Disclosure of Invention Summary

[0014] ~~The present invention provides~~ We provide a surface treated steel sheet including a steel sheet; a plating layer containing at least one metal selected from the group consisting of zinc and aluminum on at least one surface of the steel sheet; and a film on the plating layer, the film containing at least one metal selected from the group consisting of Al, Mg, and Zn, a tetravalent vanadium compound, and a phosphoric acid group.

*Kindly replace paragraph [0023] with the following:*

[0023] ~~The present invention~~ We also provides provide a method for manufacturing a surface treated steel sheet, the method including the steps of adhering a treatment solution containing at least

one metal selected from the group consisting of Al, Mg, and Zn, a tetravalent vanadium compound, and a phosphoric acid group to a plating layer containing at least one metal selected from the group consisting of zinc and aluminum, the plating layer disposed on at least one surface of a steel sheet and, thereafter, conducting drying at a peak sheet temperature of 60°C to 250°C.

*Kindly replace paragraphs [0027] to [0030] with the following:*

[0027] In addition, ~~the present invention~~ we also provides provide a surface treated steel sheet exhibiting excellent corrosion resistance and film appearance, the surface treated steel sheet characterized in that a surface treatment film containing a vanadium compound having a valence of four, a phosphoric compound, and a compound of at least one metal selected from the group consisting of Al, Mg, and Zn is disposed on a surface of a steel sheet plated with at least one type selected from the group consisting of a zinc based type, an aluminum based type, and an Al-Zn based type.

#### Best Mode for Carrying Out the Invention Detailed Description

[0028] The details of ~~the present invention~~ our steel sheets and the reasons for the limitations thereof will be described below.

[0029] The steel sheet used as a base material ~~in the present invention~~ is not specifically limited. Preferable examples thereof include a thin steel sheet and a thin steel strip from the viewpoint of the applications thereof. In general, the thicknesses of these steel sheets suitable for use are about 0.1 mm to about 3 mm.

[0030] The plating layer ~~constituting the present invention~~ is a plating layer containing at least one metal selected from the group consisting of zinc and aluminum. That is, the plating is zinc-containing plating, aluminum-containing plating, or plating containing both zinc and aluminum.

*Kindly replace paragraphs [0035] to [0038] with the following:*

[0035] Among the above-described plating, the Al-Zn alloy plating containing 25 to 75 percent by mass of aluminum is preferable since extremely excellent corrosion resistance and surface appearance are exhibited. This is because when the Al-Zn alloy plating has an Al content of 25 percent by mass or more, the corrosion resistance is improved by addition of phosphoric acid. In addition, when the Al content is 75 percent by mass or less, the adhesion of the film is increased, and peeling becomes resistant to occurrence. It is known that 55%Al-Zn alloy plating is the most representative example thereof. In general, the 55%Al-Zn alloy plating refers to alloy plating containing about 50 to 60 percent by mass of Al. In the following description of the present invention, "high-Al-Zn plating" refers to Al-Zn alloy plating having the above-described Al content. This type of plating film contains Si at a content of 0.5 percent by mass or more of the amount of Al, and about 1 to 3 percent by mass of Si is contained usually.

[0036] All plating layers of the present invention can be produced by various known plating methods, and the method is not specifically limited. That is, the plating layer can be formed by not only a hot dipping method, but also a hot dipping and alloying method (an alloying treatment is conducted after the hot dipping is conducted), an electroplating method, a vapor deposition method, or a combination thereof, on an as needed basis. Furthermore, at least two layers of the same type or different types of plating may be applied to produce multilayer plating.

[0037] ~~The inventors of the present invention~~ We conducted research on inorganic compounds which does not cause coloring, exhibits excellent surface appearance, and exhibits excellent corrosion resistance. As a result, it was found that a film appearance problem due to coloring, which had been a problem to be dissolved, was able to be overcome by using not a pentavalent vanadium compound heretofore known as a rust inhibitor of zinc and aluminum, but a tetravalent vanadium

compound. It was found that particularly excellent corrosion resistance was exhibited by the use in combination with phosphoric acid or a phosphoric acid compound. Furthermore, it was found that addition of Al, Mg, or Zn to the film exerted an effect on reducing coloring of the film appearance, while the coloring tended to occur when the film was exposed at a humid environment and the like.

[0038] ~~In the present invention,~~ a A surface treatment film containing at least one metal selected from the group consisting of Al, Mg, and Zn, a vanadium compound having a valence of four, and a phosphoric acid group is formed on a surface of the above-described plated steel sheet.

*Kindly replace paragraph [0041] with the following:*

[0041] The phosphoric acid group will be described. In general, an acid group refers to a portion remaining after at least one hydrogen atom capable of substituting for a metal is removed from the acid molecule. The phosphoric acid group ~~in the present invention~~ refers to a portion remaining after at least one hydrogen atom capable of substituting for a metal is removed from a phosphoric acid analog. Such a phosphoric acid analog refers to an acid or the like containing phosphorous. Examples thereof include a series of acids generated by various degrees of hydration of phosphorous pentoxide; orthophosphoric acid; metaphosphoric acid; condensed phosphoric acids, e.g., pyrophosphoric acid, tripolyphosphoric acid, and polyphosphoric acids; and phosphorous acid and the like, e.g., phosphorous acid and hypophosphorous acid. The phosphoric acid group ~~used in the present invention~~ is water-soluble. Examples of water-soluble phosphoric acid compounds which generate phosphoric acid groups include the above-described phosphoric acid analog and various salts thereof. At least one type of them can be used alone or in combination. When orthophosphoric acid is taken as an example, primary phosphates, secondary phosphates, tertiary phosphates, and the like correspond to the various salts. Preferably, the amount of adhesion of phosphoric acid group per one surface of the film is 5 to 800 mg/m<sup>2</sup> in terms of phosphorous. When the amount of adhesion is

5 mg/m<sup>2</sup> or more, satisfactory corrosion resistance is exhibited. On the other hand, excessive addition provides an economic disadvantage. Therefore, a guideline of an upper limit is set at 800 mg/m<sup>2</sup>. However, since the amount of phosphoric acid group also depends on the resin properties significantly, the amount of addition can be selected from these points of view.

*Kindly replace paragraph [0044] with the following:*

[0044] ~~The inventors of the present invention~~ We conducted research to find inorganic compounds for a surface treatment, the inorganic compound causing no coloring, exhibiting excellent film appearance, and exhibiting excellent corrosion resistance. As a result, it was found that particularly excellent corrosion resistance was exhibited by forming a film composed of a tetravalent vanadium compound and a phosphoric acid group on a surface of the above-described plated steel sheet. This film was able to be formed by applying a surface treatment solution in which the tetravalent vanadium compound and phosphoric acid are blended and, thereafter, conducting drying. However, the film composed of the tetravalent vanadium compound and phosphoric acid exhibited unsatisfactory dissolution resistance. It was made clear that there were problems. For example, when a film was stacked in a wet state, a part of the film was dissolved to cause variations in appearance, and the adhesion of film was deteriorated due to wetting, so that the film was readily peeled off.

*Kindly replace paragraph [0046] with the following:*

[0046] That is, the at least one metal selected from the group consisting of Zn, Al, and Mg ~~in the present invention~~ includes an ion, a simple substance, and/or a compound of the metal. The compound of the metal is not specifically limited. The simultaneous presence of metals and metal compounds other than this in the film of the ~~present invention~~ is not excluded. However, as a matter of course, ~~from the purport of the present invention~~ to prevent [[the]] pollution, chromium and

chromium compounds are excluded. This is because a chromium-free film is thereby produced.

***Kindly replace paragraphs [0050] and [0051] with the following:***

[0050] On the other hand, the tetravalent vanadium compound used in the present invention effects weak oxidation in contrast to the pentavalent vanadium compound. Therefore, divalent and trivalent vanadium compounds are resistant to forming, and most of tetravalent vanadium compounds remain tetravalent and are contained in the film. It is believed that the resulting tetravalent vanadium compounds exhibit the corrosion resistance. The reason the tetravalent vanadium compound exerts an adequate barrier effect is assumed that a tetravalent vanadyl(IV) ion:  $\text{VO}_2^+$  and a complex ion thereof (for example,  $[\text{VO}(\text{SO}_4)_2]^{2-}$ ) form a dense film on the plating surface as compared with other compounds. According to ~~[[the]]~~ our experiments ~~conducted by the inventors of the present invention~~, most of the tetravalent vanadium compounds used remained tetravalent actually in the formed film. Therefore, ~~in the present invention~~, it is an adequate level that 70 percent by mass or more of vanadium in the film is tetravalent. Preferably, it is 80 percent by mass or more, and more preferably is 95 percent by mass or more. These can be determined from the area ratio of each peak, on a valence basis, resulting from resolution of the 2p peak of vanadium obtained by X-ray photoelectron spectroscopy.

[0051] ~~In the present invention, the corrosion~~ Corrosion resistance can be dramatically improved by adding a phosphoric acid compound and the tetravalent vanadium compound in combination. It is believed that an interfacial reaction between the treatment solution and the metal is responsible therefor since the corrosion resistance is improved regardless of the surface condition of the plated steel sheet. That is, it is assumed that the etching reaction on the plating surface is increased by blending the phosphoric acid compound in the surface treatment film. An interfacial reaction layer containing vanadium and phosphorous is formed on the surface of the plating layer activated by this

etching reaction, and a dense film firmly adhered to the plating metal is formed.

***Kindly replace paragraphs [0053] and [0054] with the following:***

[0053] Additional components other than the above-described components, for example, at least one of Ca, Ca based compounds,  $\text{SiO}_2$ , other silicic acid based compounds, Ta, Nb, Ta based compounds, and Nb based compounds can be added to the surface treatment film ~~of the present invention~~. These components are added in order to further improve the corrosion resistance. For example, sodium silicate and calcium carbonate are appropriately added to a phosphoric acid compound (zinc phosphate, zinc polyphosphate, aluminum tripolyphosphate, or the like) in a dispersed state in water, the resulting deposits are washed with water, and the residue from which soluble components have been removed can be used as this additive. Colloidal silica (wet-process silica) or dry-process silica can be used as  $\text{SiO}_2$ . Ta and Nb can be added as fluorides and the like. The types and addition methods of these compounds are not specifically limited.

[0054] At least one compound selected from oxide fine particles (for example, silicon oxide, aluminum oxide, zirconium oxide, titanium oxide, cerium oxide, and antimony oxide), phosphates (for example, zinc phosphate, aluminum dihydrogen phosphate, and zinc phosphite), molybdates, phosphomolybdates (aluminum phosphomolybdate and the like), vanadates, organic phosphoric acids and salts thereof (for example, phytic acid, phytates, phosphonic acid, phosphonates, and metal salts thereof, and alkali metal salts), organic inhibitors (for example, hydrazine derivatives, thiol compounds, and dithiocarbamates), organic compounds (polyethylene glycol), and the like serving as a rust inhibitor to improve the corrosion resistance may be further added to the surface treatment film ~~of the present invention~~.

***Kindly replace paragraphs [0056] and [0057] with the following:***

[0056] The film ~~of the present invention~~ is produced by a method including the steps of adhering



a Cr-free treatment solution containing at least one metal selected from the group consisting of Al, Mg, and Zn, a tetravalent vanadium compound, and a phosphoric acid group to a plating layer containing at least one metal selected from the group consisting of zinc and aluminum, the plating layer disposed on at least one surface of a steel sheet, and thereafter, conducting drying at a peak sheet temperature of 60°C to 250°C.

[0057] The method for forming the surface treatment film on a surface of the plated steel sheet may be a usually adopted method. In a method for adhering the treatment solution, for example, a surface treatment composition ~~within the scope of the present invention~~ is treated by a coating method, an immersion method, a spraying method, or the like and, thereafter, heat-drying is conducted. The coating treatment method is any one of methods of a combination of spraying and roll-squeezing, a roll coater (three-roll system, two-roll system, and the like), a squeeze coater, and the like. Alternatively, it is also possible to adjust the amount of coating by an air knife method or a roll-squeezing method, ensure uniform appearance, and ensure uniform film thickness after the coating treatment with the squeeze coater or the like, the immersion treatment, or the spraying treatment is conducted. For example, a dryer, a hot-air oven, a high-frequency induction furnace, an electric furnace, an infrared furnace, and the like can be used as the heat-drying device.

*Kindly replace paragraphs [0059] to [0061] with the following:*

[0059] It is desirable that the thickness of the surface treatment film ~~in the present invention~~ is 5  $\mu\text{m}$  or less after the above-described heat-drying. When the thickness is 5  $\mu\text{m}$  or less, the film is formed satisfactorily during even a low-temperature drying and, therefore, the corrosion resistance is improved. Preferably, the thickness is 3  $\mu\text{m}$  or less, and more preferably is 2  $\mu\text{m}$  or less.

[0060] A surface treated steel sheet exhibiting excellent corrosion resistance and surface appearance can be produced by the surface treatment film formed as described above. However, in

~~the present invention~~, an organic resin is further blended into the surface treatment film. Alternatively, an organic resin coating layer can be further disposed on the surface treatment film. The film can exhibit further improved corrosion resistance by this organic resin, and at the same time, the film can also exhibit excellent surface appearance and workability in combination.

[0061] The film further containing the organic resin is produced by further adding an organic resin to the treatment solution in the above-described manufacturing method. Conversely, the components of the treatment solution may be added to a dispersion or solution of the organic resin, as a matter of course. However, since it is preferable that the treatment solution of ~~the present invention~~ is an aqueous solution, preferably the organic resin to be used is water-soluble or water-dispersible. In every case, preferably the amount of adhesion of organic resin per one surface is 0.5 to 5 g/m<sup>2</sup>. When the amount of adhesion of organic resin is 0.5 g/m<sup>2</sup> or more, the workability is improved and galling of plating by working can be prevented. On the other hand, when the amount of adhesion of organic resin is controlled at 5 g/m<sup>2</sup> or less, the film does not adhere to the roll during roll forming and, therefore, this is preferable. From the above-described viewpoint, a more preferable range of the amount of adhesion of organic resin is 1.0 to 4.5 g/m<sup>2</sup>, and 1.5 to 4 g/m<sup>2</sup> is further desirable.

*Kindly replace paragraph [0077] with the following:*

[0077] In the above description, examples of various organic resins allowed to be present in the film or on the film of ~~the present invention~~ are shown. Most of all, the following organic resins are particularly preferable since the corrosion resistance, the appearance quality, and the workability are mutually compatible and outstanding performance is delivered with respect to all of them.

***Kindly replace paragraph [0079] with the following:***

[0079] Preferably, the copolymer resin has a solid content of styrene (a) of 20 to 60 percent by mass, a solid content of (meth)acrylic acid (b) of 0.5 to 10 percent by mass, and a solid content of (meth)acrylic ester (c) including an alkyl chain having the carbon number of 1 to 6 of 20 to 60 percent by mass relative to 100 percent by mass of solid content of the copolymer resin. ~~In the present invention, the~~ The "solid content" is defined as a solid content of a product after being dried at a peak sheet temperature of 60°C to 250°C regardless of whether the organic resin is present in the film or on the film. In general, such a drying takes on the order of 30 minutes. The amount of the above-described solid content can be measured by methods of infrared spectroscopy, gas chromatography-mass spectrometry, and the like.

***Kindly replace paragraph [0085] with the following:***

[0085] If necessary, each of the above-described organic resins ~~used in the present invention~~ can be blended with a solid lubricant for the purpose of improving the workability of the film. Such a solid lubricant is not specifically limited. Examples thereof can include aliphatic acid ester wax that is a product resulting from esterification of a polyol compound and an aliphatic acid, silicon based wax, fluorine based wax, polyolefin wax, e.g., polyethylene, lanolin based wax, montan wax, microcrystalline wax, and carnaúba wax. At least one of the solid lubricants can be used alone or in combination. The amount of blending of the solid lubricant is specified to be 1 to 50 parts by mass (solids) relative to 100 parts by mass (solids) of resin, and preferably be 3 to 30 parts by mass (solids). When the amount of blending of the solid lubricant is 1 part by mass or more, a lubricating effect is exerted. On the other hand, it is preferable that the amount of blending is 50 parts by mass or less since the paintability is improved. Furthermore, it is desirable that the film contains the above-described curing agent, a rust inhibitor, or the like from the viewpoint of an improvement of

the corrosion resistance.

***Kindly replace paragraph [0098] with the following:***

[0098] The surface treated steel sheet of the present invention exhibits excellent corrosion resistance and excellent surface appearance without containing substances, such as chromium, harmful to the human body and the environment in the surface treatment film. Therefore, the manufacturing process thereof can be made pollution-free. In addition, the resulting surface treated steel sheet is an environment-conscious surface treated steel sheet, and can be widely used for automobiles, household electrical appliances, construction materials, and the like.